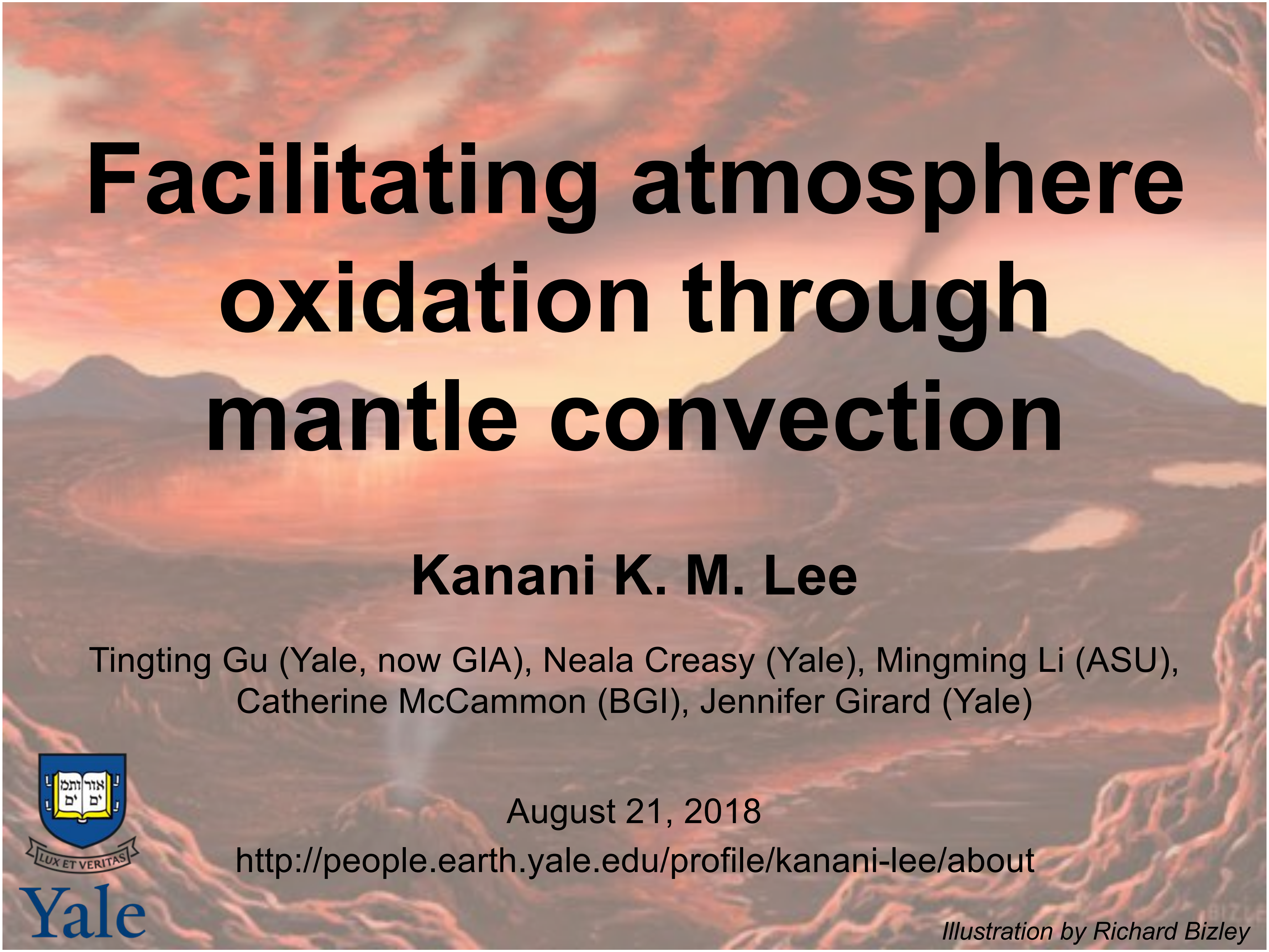

Facilitating atmosphere oxidation through mantle convection

Kanani K. M. Lee

Tingting Gu (Yale, now GIA), Neala Creasy (Yale), Mingming Li (ASU), Catherine McCammon (BGI), Jennifer Girard (Yale)

Yale

August 21, 2018

http://people.earth.yale.edu/profile/kanani-lee/about

Illustration by Richard Bizley

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T. Gu
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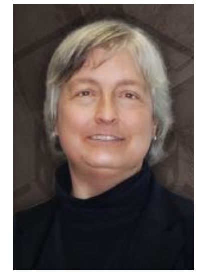
N. Creasy
(Yale)

M. Li
(ASU)



C. McCammon
(BGI)

J. Girard
(Yale)

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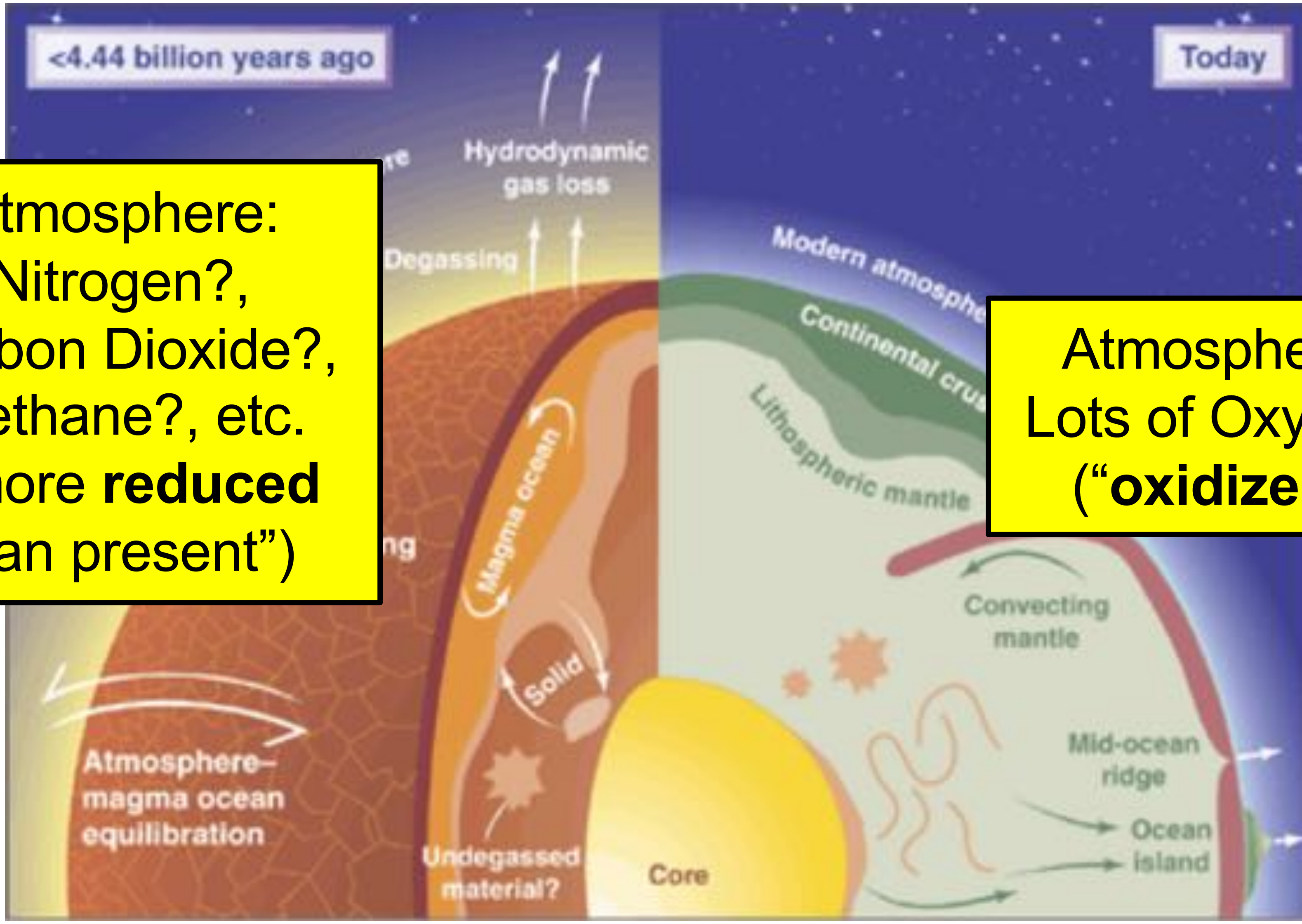
Evolution of O_2 in Atmosphere

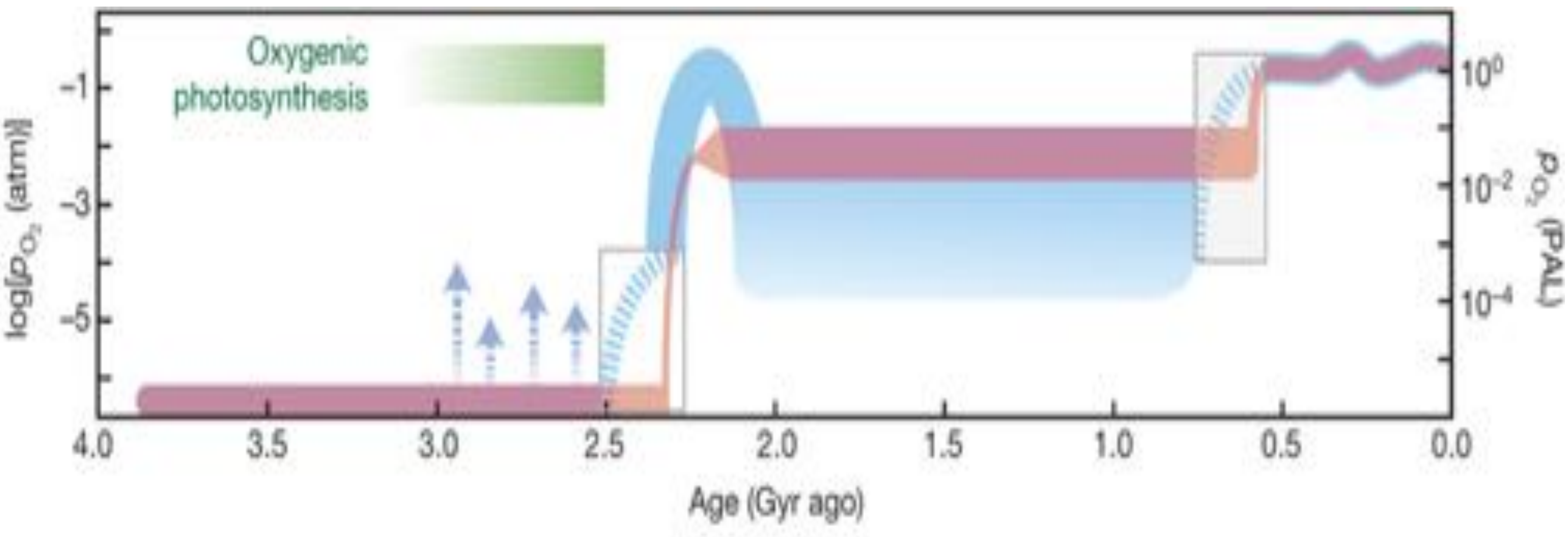


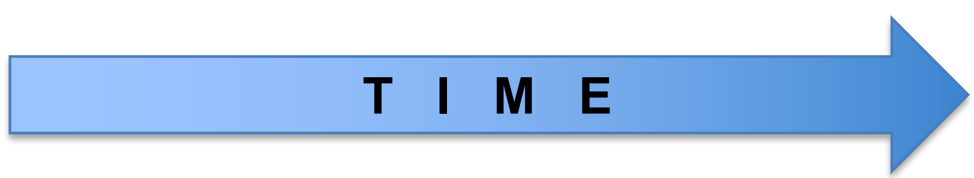
Atmosphere:
Nitrogen?,
Carbon Dioxide?,
Methane?, etc.
("more **reduced** than present")

Atmosphere:
Lots of Oxygen!
("**oxidized**")

Ballentine, 2002

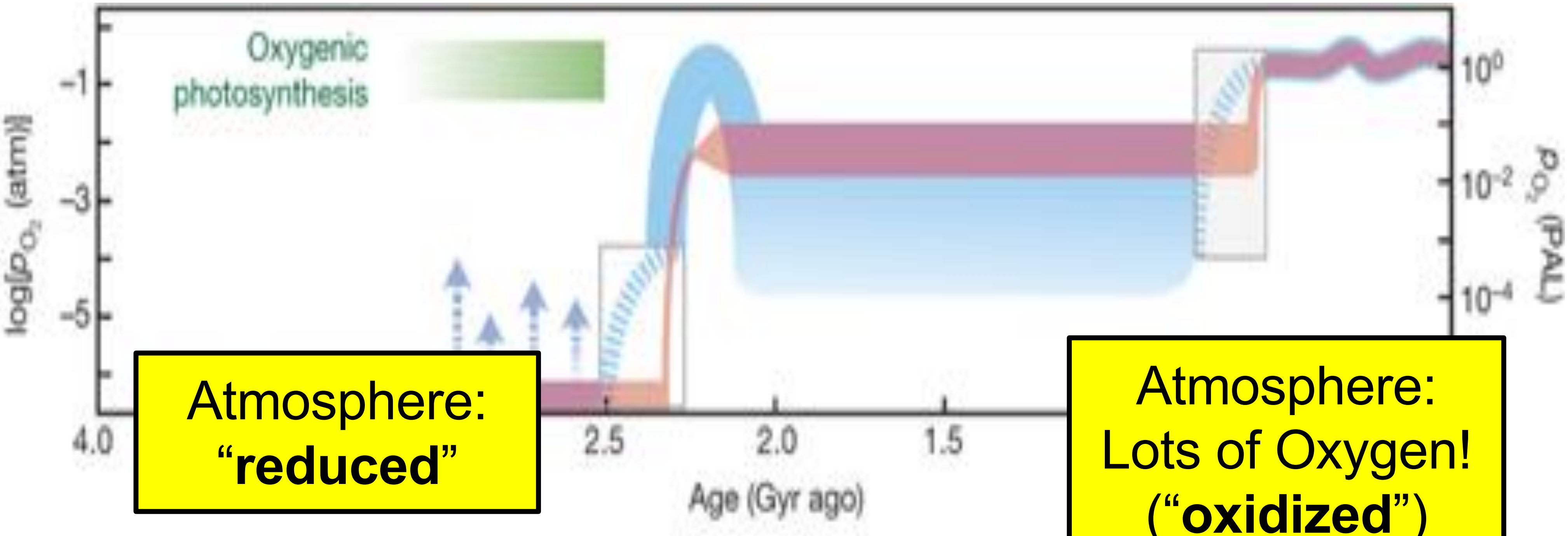
Evolution of O_2 in Atmosphere





Lyons et al., 2014

Evolution of O_2 in Atmosphere



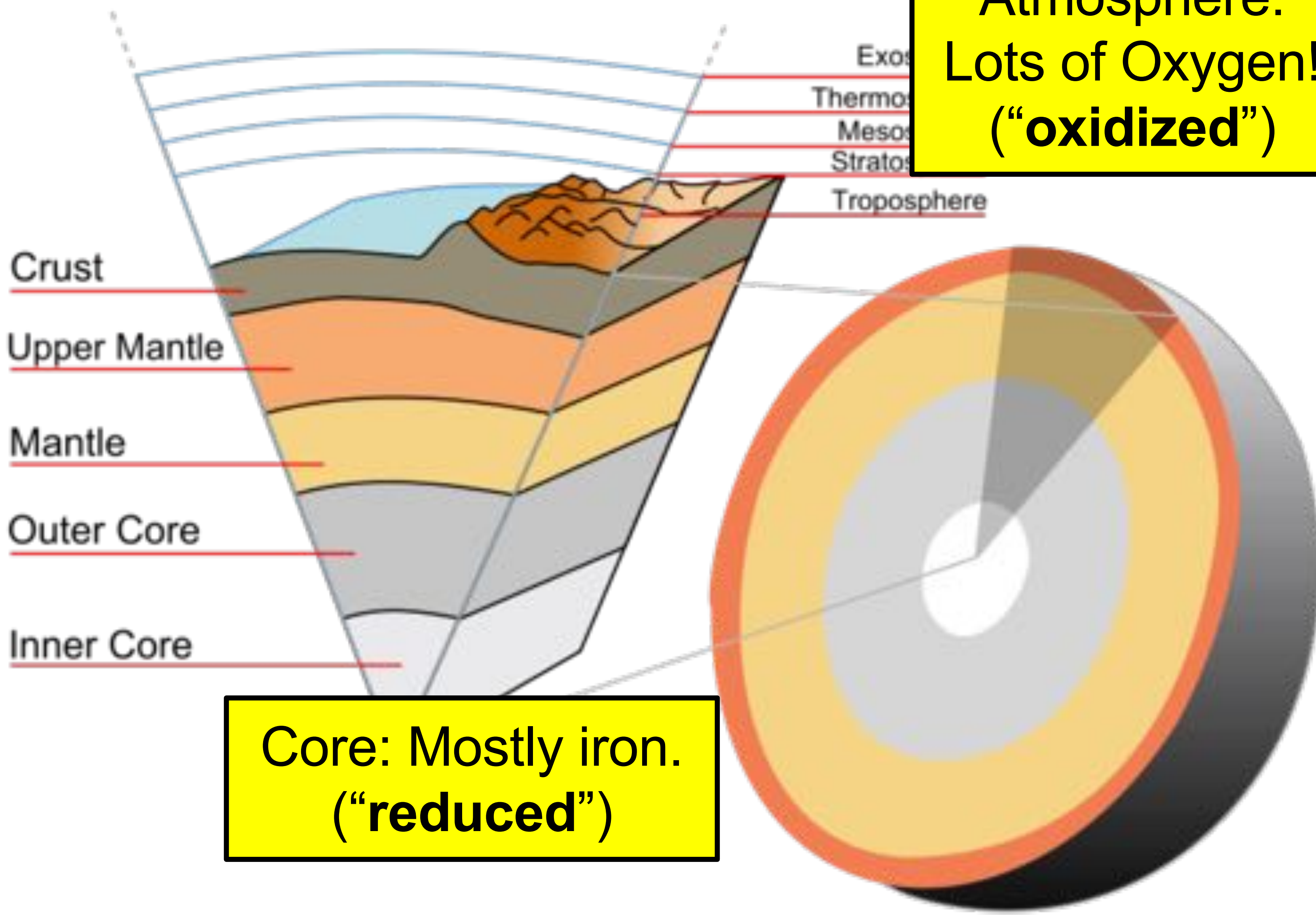
Atmosphere:
“**reduced**”

Atmosphere:
Lots of Oxygen!
(“**oxidized**”)

T I M E

Lyons et al., 2014

Earth Structure

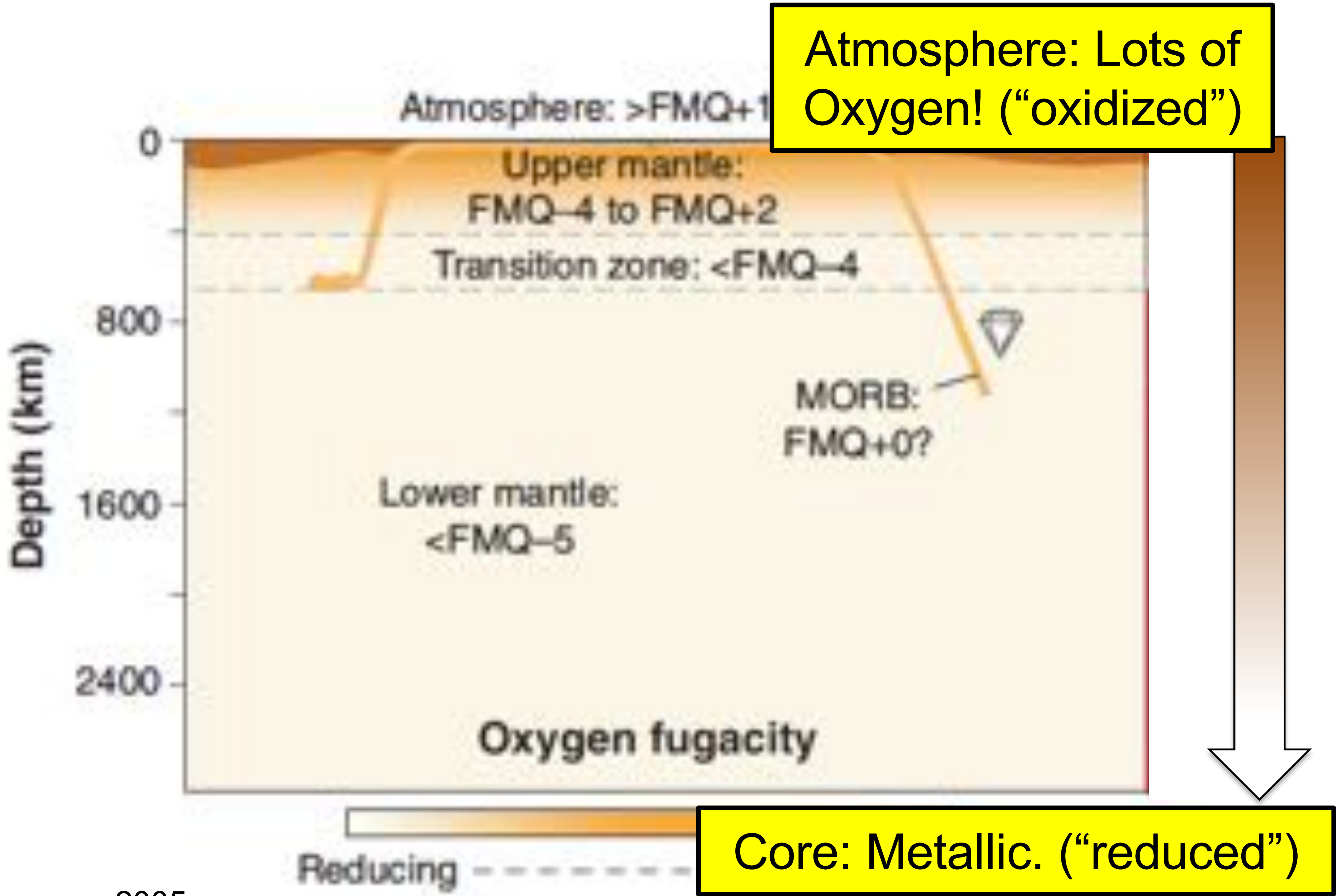


Atmosphere:
Lots of Oxygen!
(“**oxidized**”)

Core: Mostly iron.
(“**reduced**”)

http://www.geography.learnontheinternet.co.uk/topics/structureofearth.html

Oxygen Fugacity in the Mantle

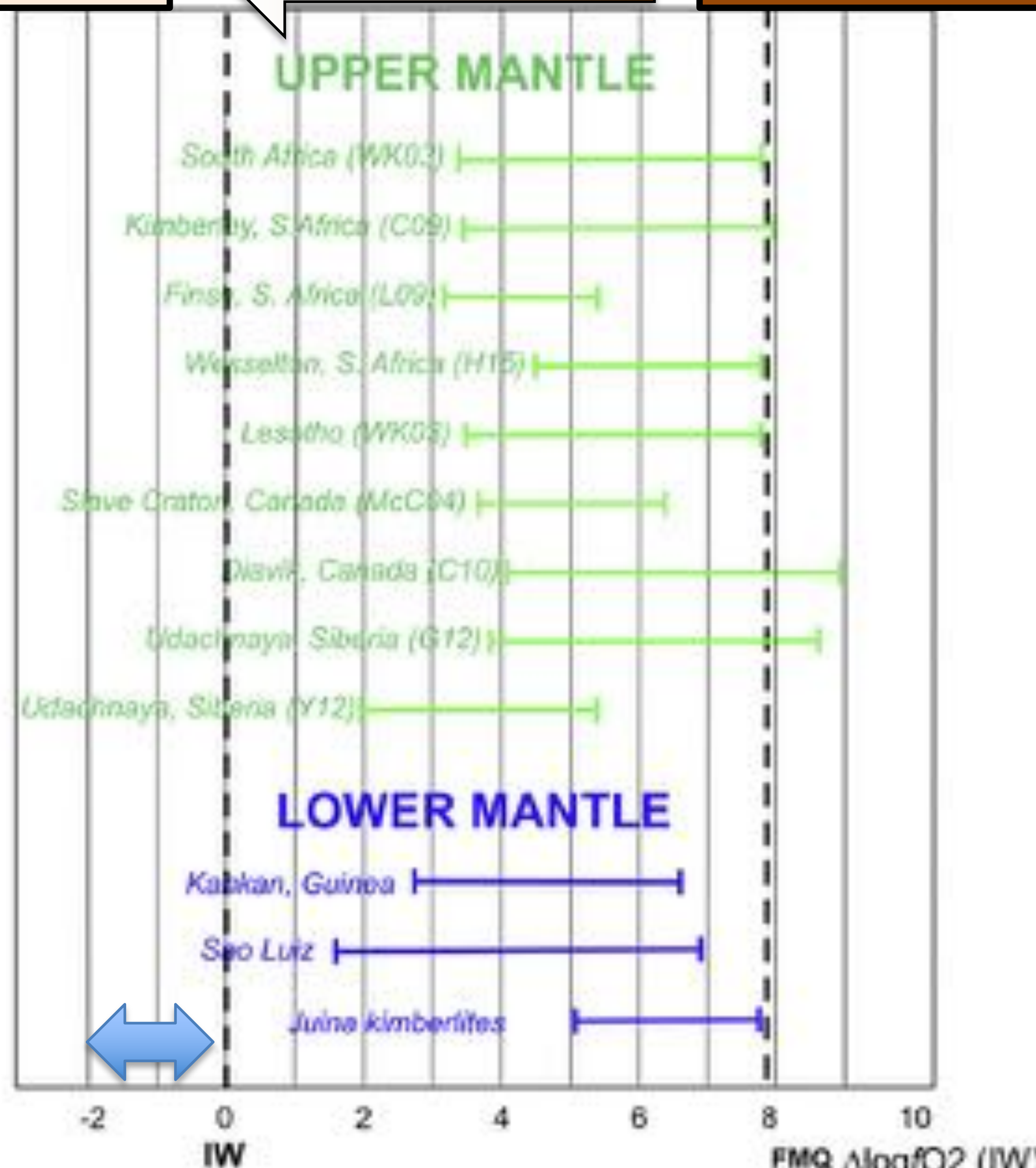


McCammon, 2005

Oxygen Fugacity in the Mantle?

More reduced ← More oxidized

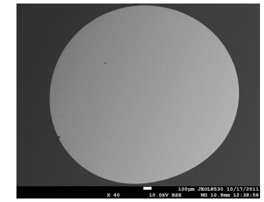
What are diamond inclusions telling us about mantle redox spatially as well as temporally?



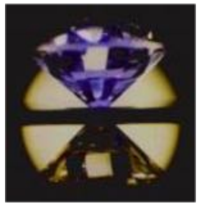
"Deep" LM inclusions

Kaminsky, 2011, 2015

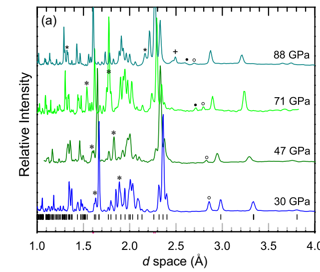
Methods



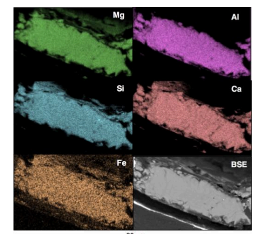
- **Synthesize** LM glasses: differ only in Fe^{3+} content
- **LHDAC**



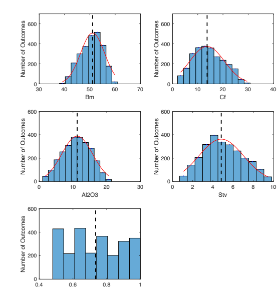
- **XRD**: identify minerals, equations of state



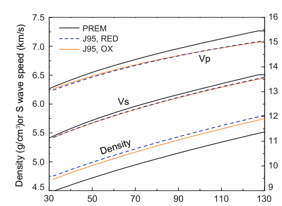
- **FIB** and **EPMA**: reveal compositions



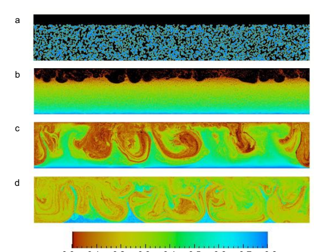
- **Monte Carlo** Method: determine abundance



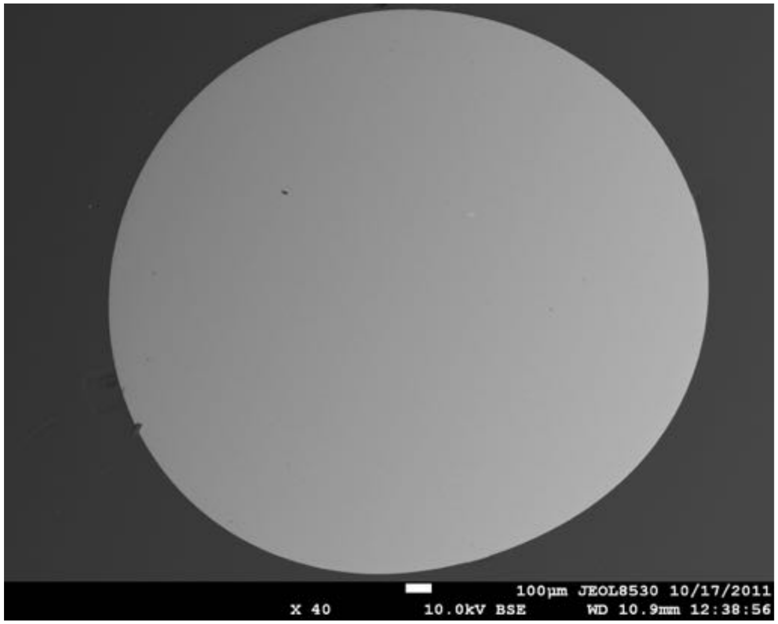
- **BURNMAN**: Compare with **PREM**

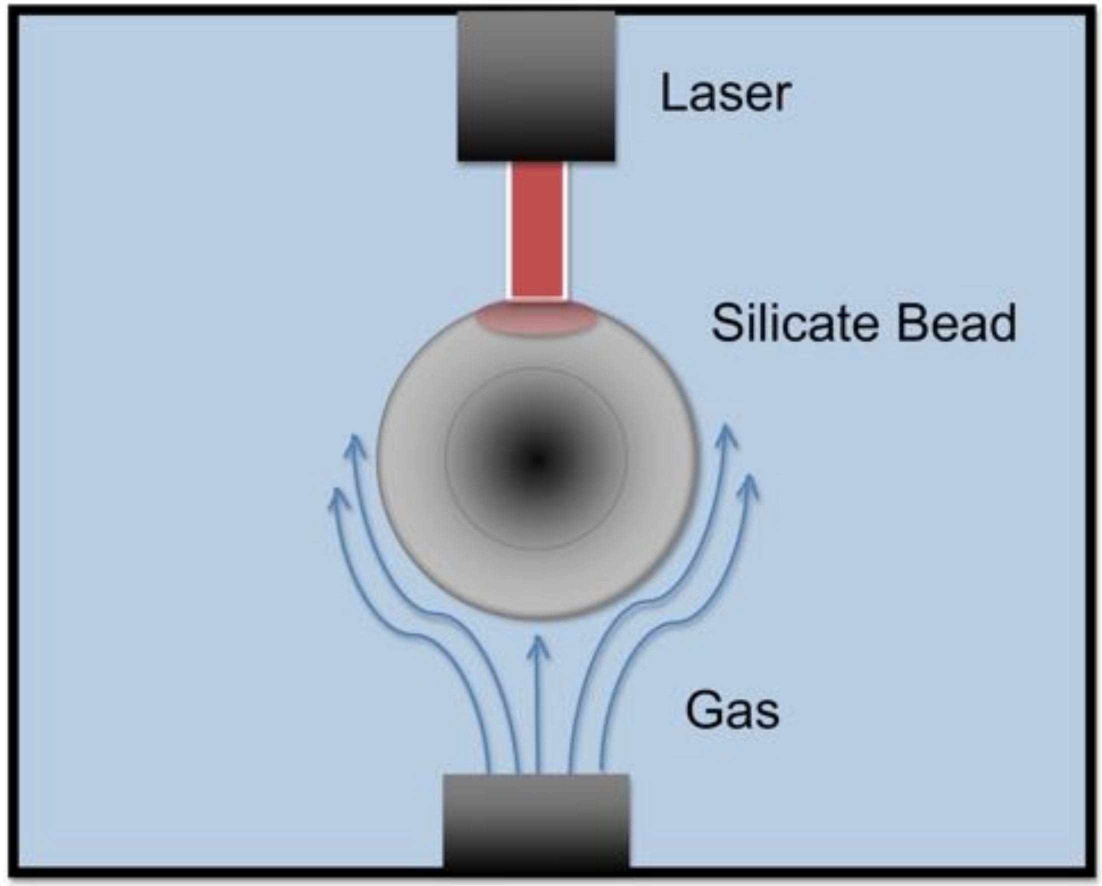


- **CITCOM** convection simulations



Starting Sample Synthesis



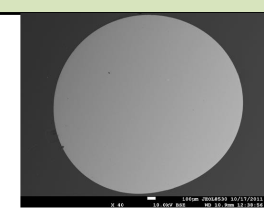


Temperature	2100-2600 K
Levitation gas	OXIDIZED: 100% O_2 REDUCED: 95% Ar, 4% CO, 1% CO_2
Composition	**J95**: Javoy, 1995 (Enstatite Lower Mantle Model) **MIX1G**: Hirschmann et al., 2003 (pyroxenite mixture and plausible OIB source

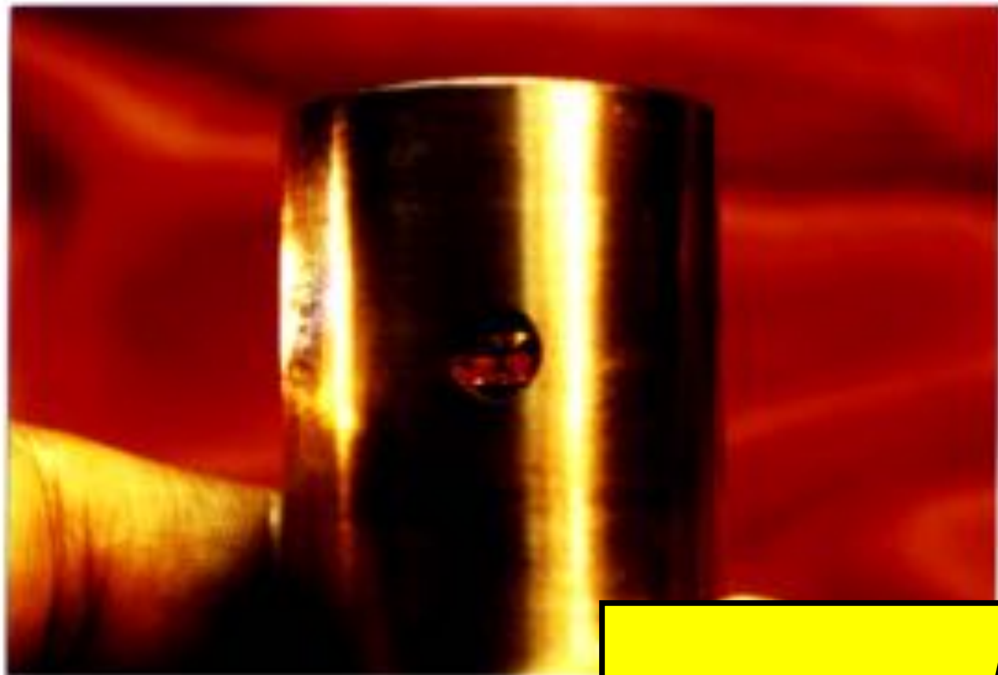
Mantle Compositions (in mol%)

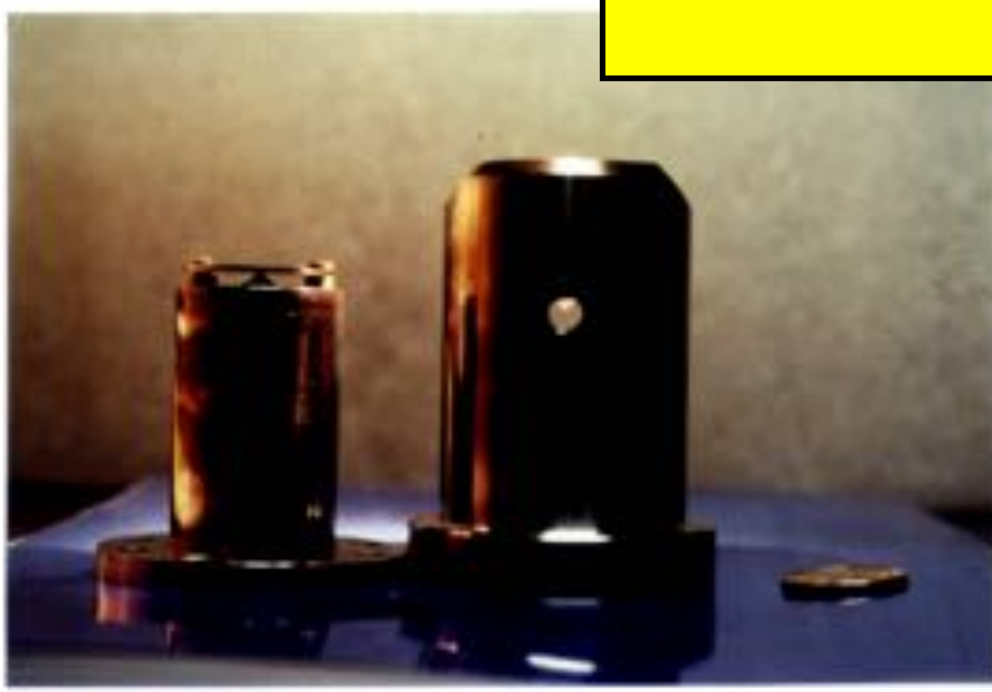
MgO	SiO_2	Al_2O_3	CaO	FeO^	Molar Mass (g/mol)	Fe^{3+}/Fe	Reference
36.9	47.3	1.2	1.7	12.9	54.79	0.30 (±0.04)	This study, J95 REDUCED [Gu et al., 2016]
37.1	47.3	1.2	1.6	12.7	54.70	0.35 (±0.04)	This study, J95 OXIDIZED [Gu et al., 2016]
37.1	47.7	1.1	1.7	12.5	54.67	NA	Enstatite Chondrite LM, [Javoy, 1995]
27.1	41.6	13.0	10.3	8.0	60.72	0.11 (±0.03)	This study, MIX REDUCED [Creasy et al., *in review*]
28.5	40.3	12.9	10.5	7.8	60.35	0.55 (±0.04)	This study, MIX OXIDIZED [Creasy et al., *in review*]
25.3	46.4	9.1	12.5	6.7	59.18	NA	MIX1G pyroxenite [Hirschmann et al., 2003]
49.4	39.2	2.3	3.3	5.8	51.83	NA	Pyrolite, [McDonough & Sun, 1995]

^All Fe is listed as FeO.

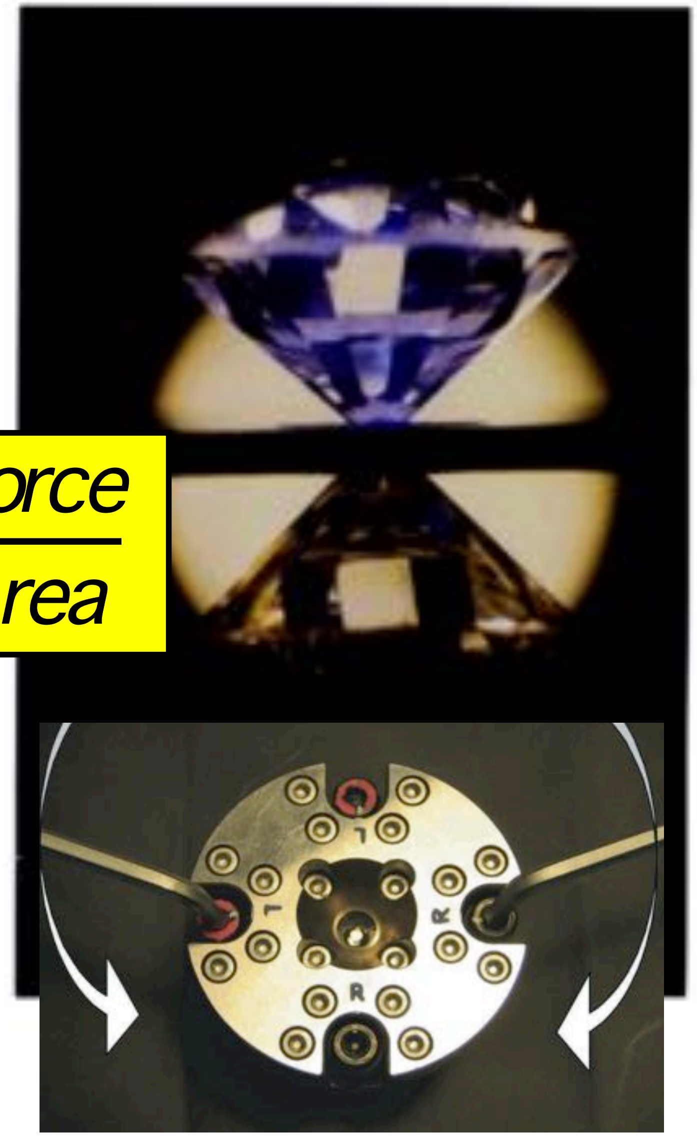


DIAMOND ANVIL CELL





$$\text{Pressure} = \frac{Force}{Area}$$

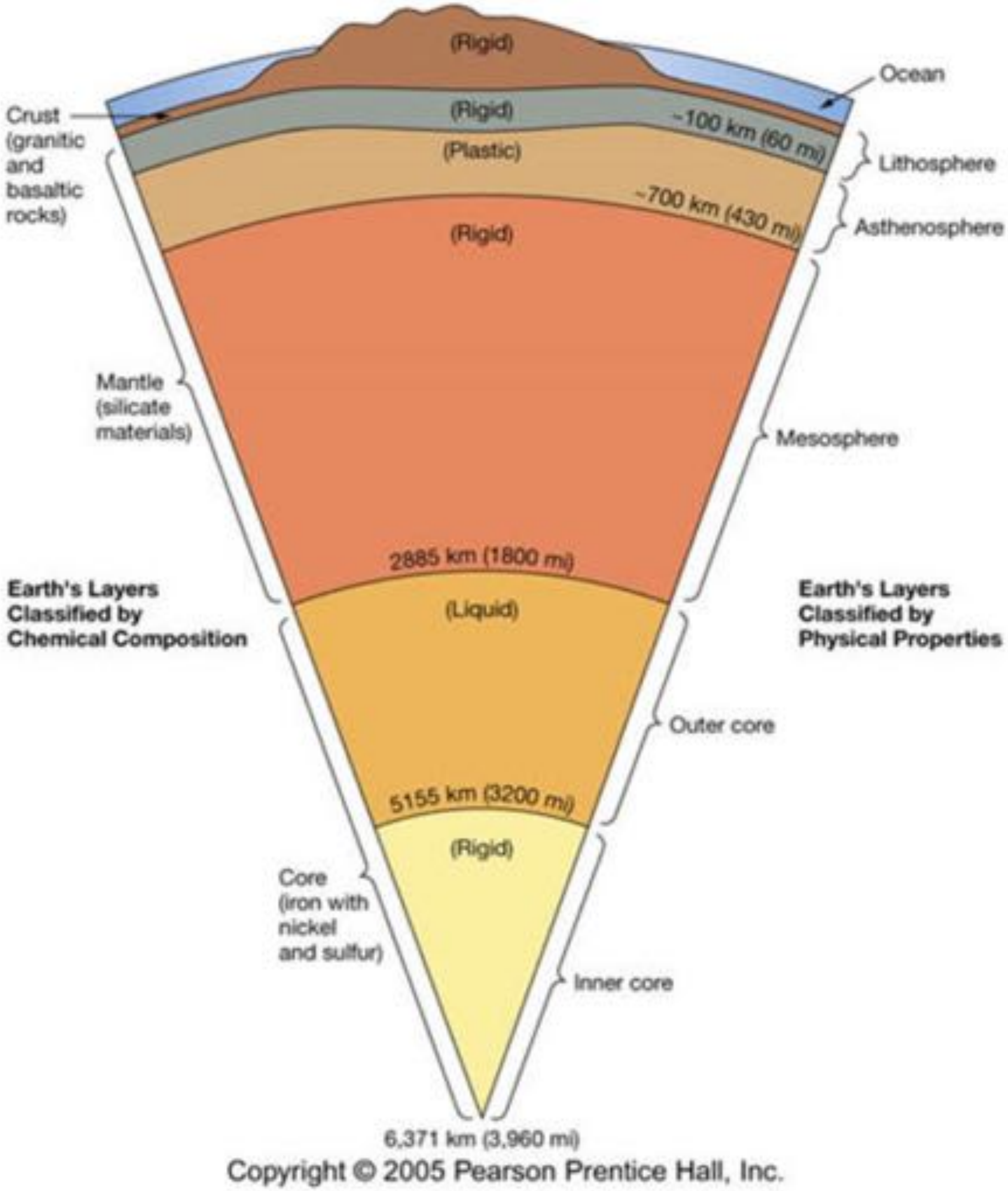


Diamond

- Strength
- Transparency


~700 African elephants → highest pressures in the Earth

Earth's current P/T conditions



0 GPa, 300 K

24 GPa, ~2000 K

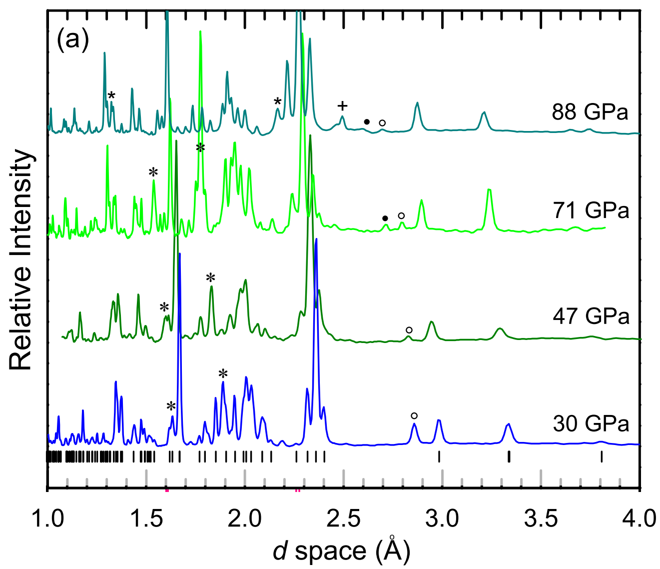
136 GPa, ~4000 K ?

330 GPa, ~6000 K ?

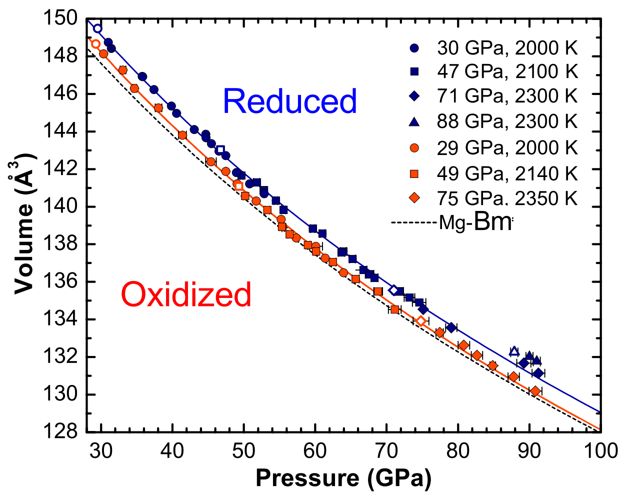
364 GPa, ~6000 K

Effect of Redox on Mantle Mineralogy: J95

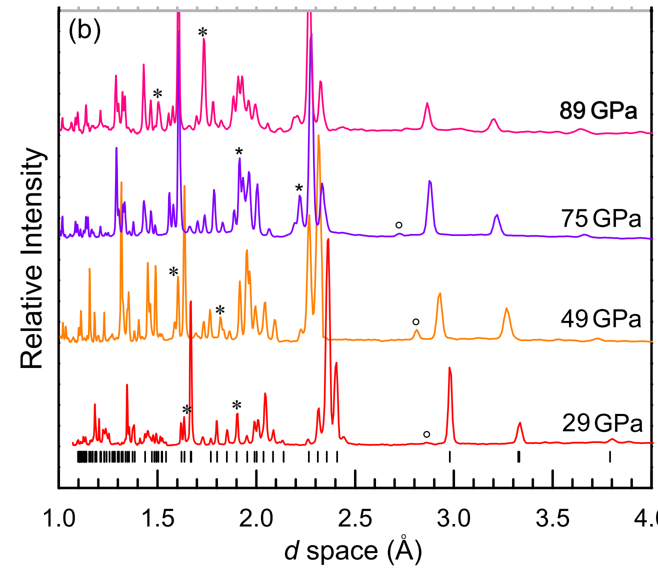
Reduced En Chon LM (Fe^{+3}/Fe ~ 30%):



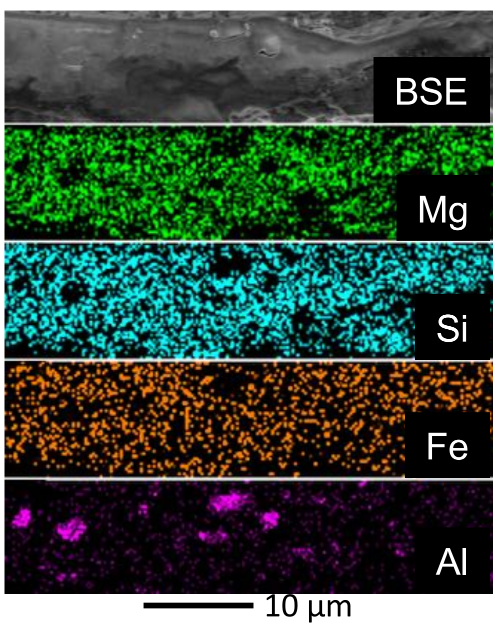
94% Bridgmanite, 5% Silica
1% Alumina



Oxidized En Chon LM (Fe^{+3}/Fe ~ 35%):

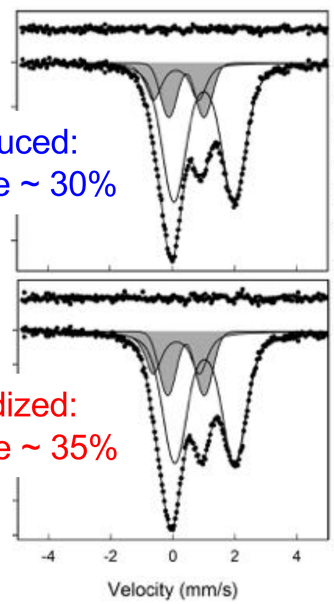


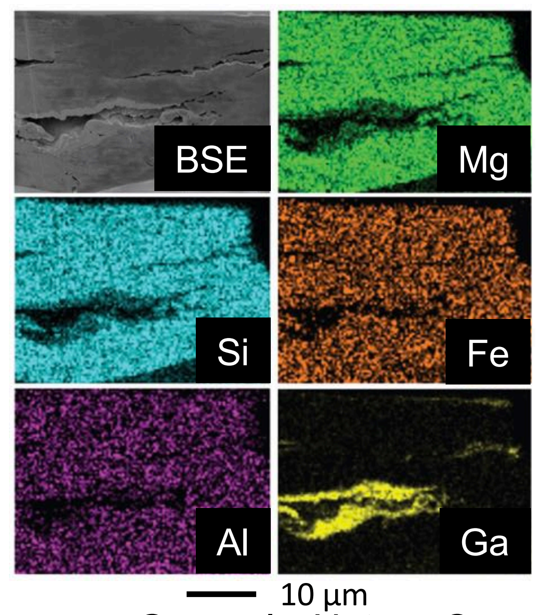
98% Bridgmanite, 2% Silica



Reduced:
Fe^{3+}/Fe ~ 30%

Oxidized:
Fe^{3+}/Fe ~ 35%



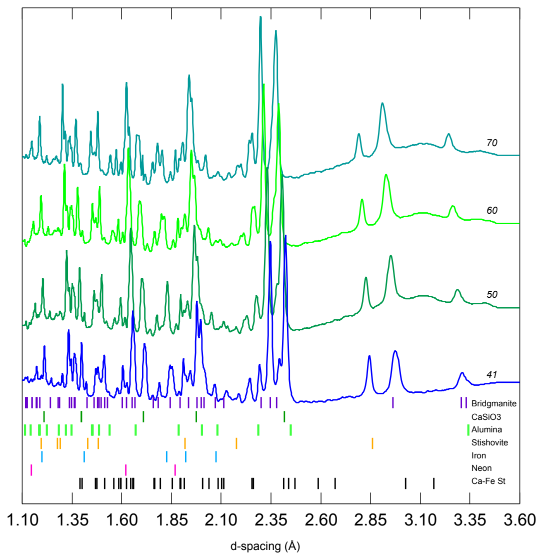


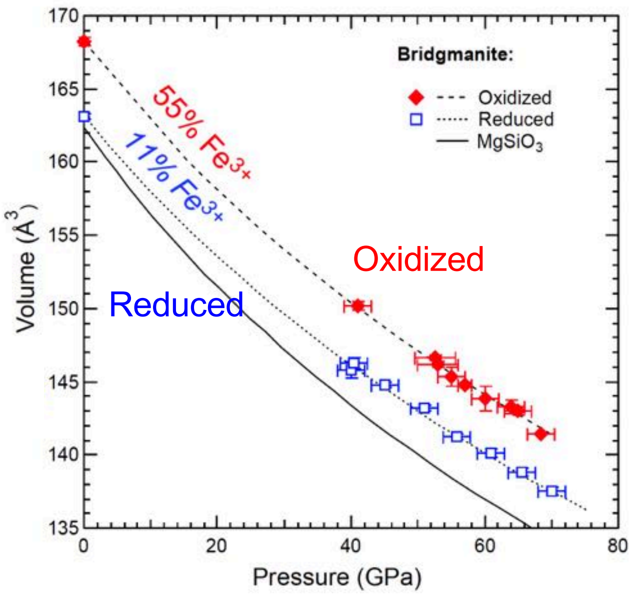
Gu et al., *Nature Geo, 2016*

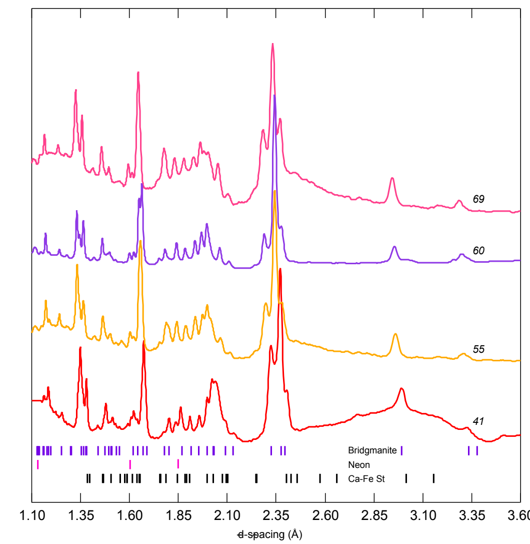
Effect of Redox on Mantle Mineralogy: MIX1G

Reduced Pyroxenite (Fe^{+3}/Fe ~ 11%):

Oxidized Pyroxenite (Fe^{+3}/Fe ~ 55%):

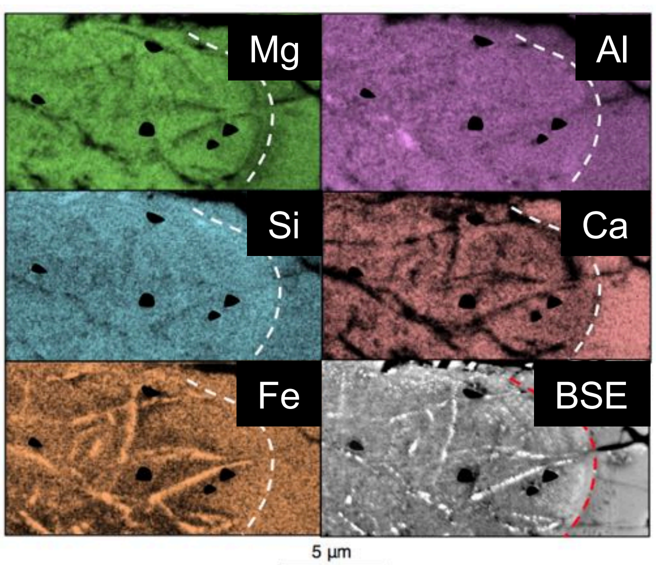






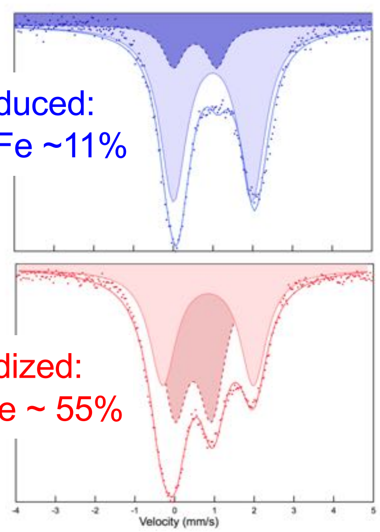
Bridgmanite (51%), Calcium perovskite (18%), CF (14%), Alumina (11%), Stishovite (5%), Iron (1%)

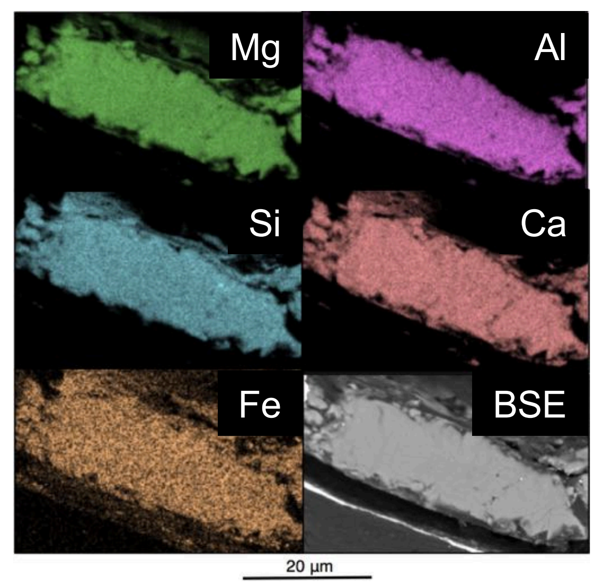
Bridgmanite (100%)



Reduced: Fe^{3+}/Fe ~11%

Oxidized: Fe^{3+}/Fe ~ 55%





Creasy et al., *under review*

Monte Carlo Modeling Mantle Mineralogy

Assumptions used for the reduced MIX1G samples

6 possible phases: Bm, Capv, Cf, Al, Stv, and Fe

Si bearing phases: Bm, Capv, Stv
Mg bearing phases: Bm, Cf
Al bearing phases: Bm, Cf, Al
Fe^0 bearing phases: Fe
Fe^{2+} bearing phases: Bm, Cf
Fe^{3+} bearing phases: Bm
Ca bearing phase: Capv

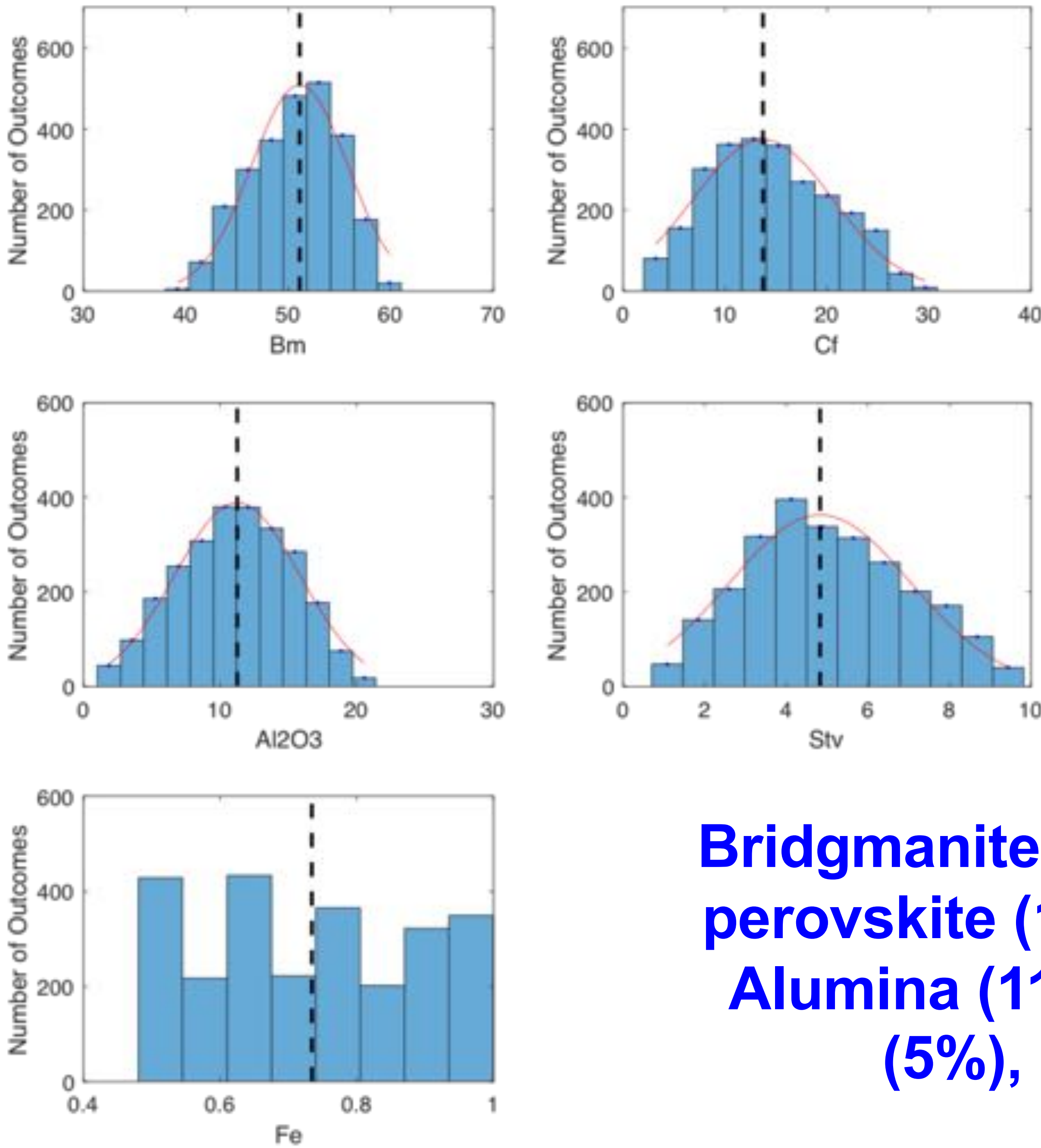
Unknowns

Distribution of Al between Bm, Al and Cf
Distribution of Si between Bm and Stv
Distribution of Mg between Bm and Cf
Distribution of Fe^{2+} between Bm and Cf
Amount of Fe^{2+} disproportionation: $3Fe^{2+} = 2Fe^{3+} + Fe^0$

Constraints

(1) Each mineral is charge balanced
(2) Self-reduction of iron occurred (we observe the presence of metallic Fe)
(3) Capv is the only calcium-bearing phase for the MIX_RED samples
(4) Cf phase is a solid solution between $MgAl_2O_4$ and $FeAl_2O_4$
(5) Use the measured Bm V_0 and existing literature to estimate volume expansion due to cation incorporation
(6) Assume all Fe^{3+} is incorporated in Bm
(7) Total Fe^{3+} content cannot exceed 55%
(8) Metallic iron is present between 0.5 to 1.0% based on EPMA results

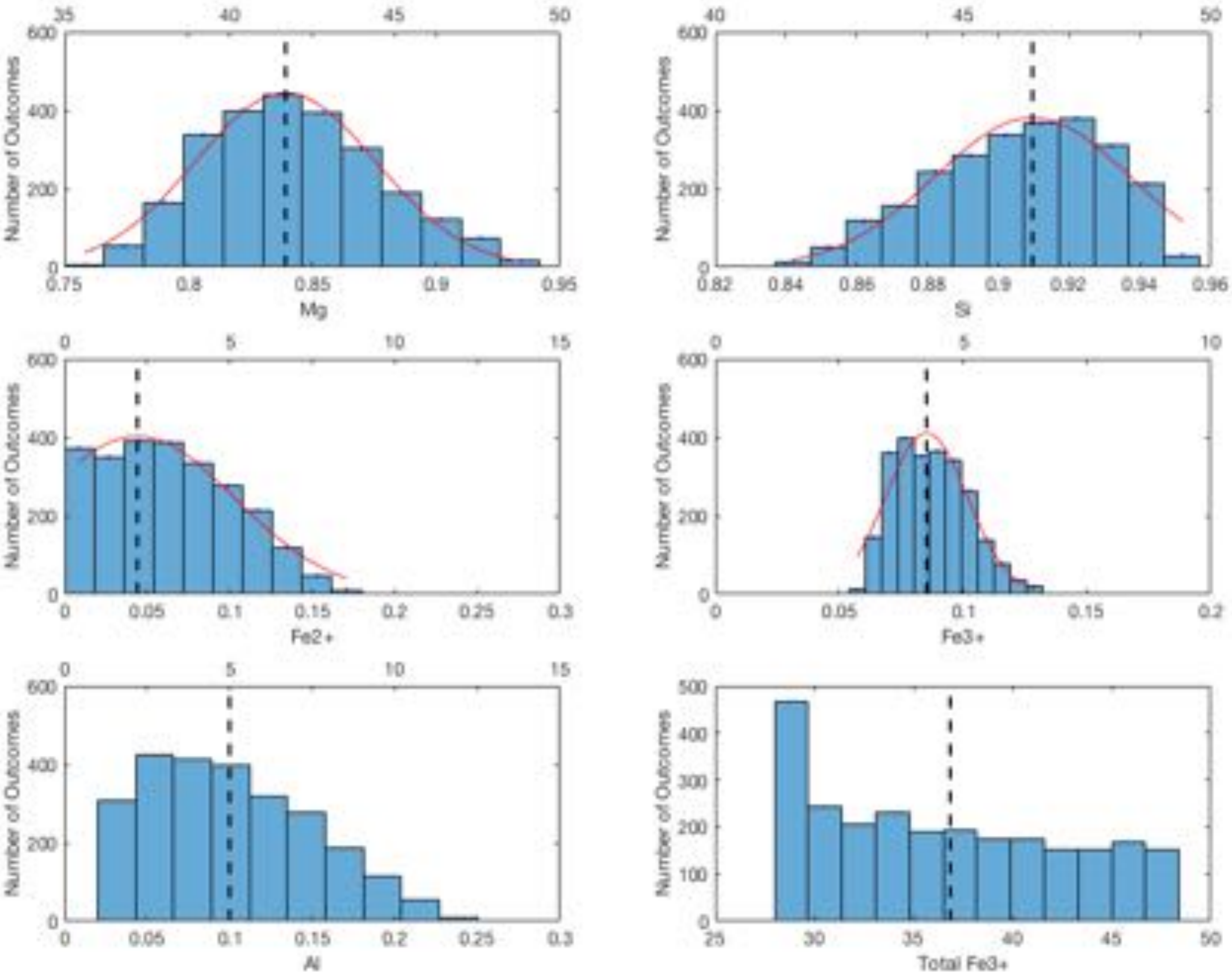
Monte Carlo Modeling Mantle Mineralogy, II



Monte Carlo results for estimating the composition of the synthesized MIX_RED: ~**3,000** possible compositions from **3 million iterations**

Bridgmanite (51%), Calcium perovskite (18%), CF (14%), Alumina (11%), Stishovite (5%), Iron (1%)

Monte Carlo Modeling Mantle Mineralogy, III



Monte Carlo results for estimating the composition of the synthesized MIX_RED: ~**3,000** possible compositions from **3 million iterations**

MIX_RED Bridgmanite composition:

$$\left(Mg_{0.84}Fe^{2+}_{0.06}Al_{0.10}Fe^{3+}_{0.09}Si_{0.91}\right)O_3$$

Comparing Bridgmanite Compositions

MIX_RED Bridgmanite composition:

$$\left(Mg_{0.84}Fe^{2+}_{0.06}Al_{0.10}Fe^{3+}_{0.09}Si_{0.91}\right)O_3$$

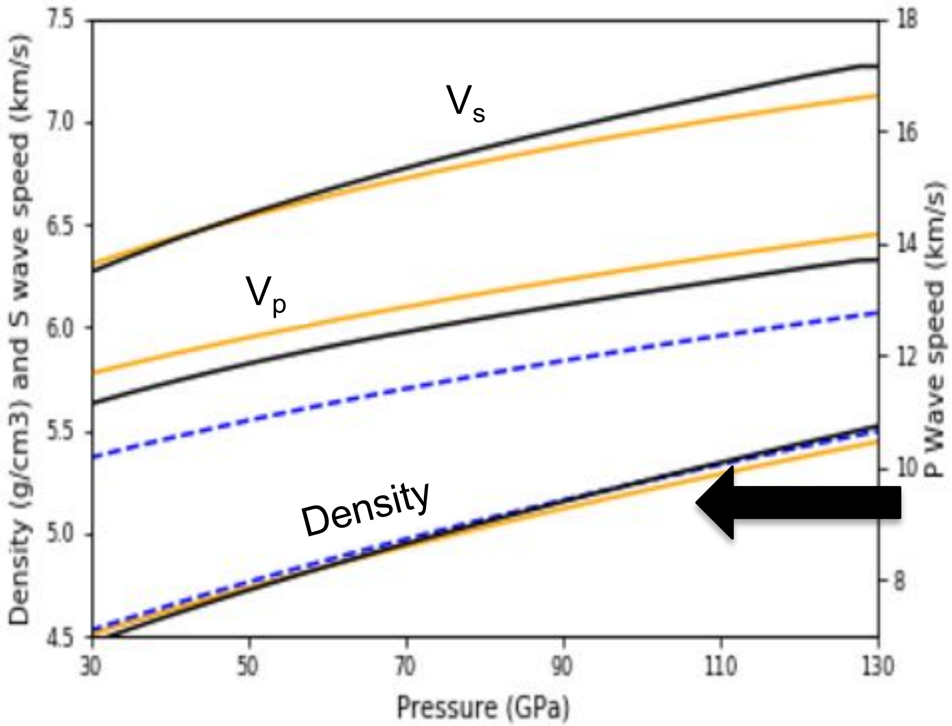
V_0= 163.6 (±0.5) Å^3

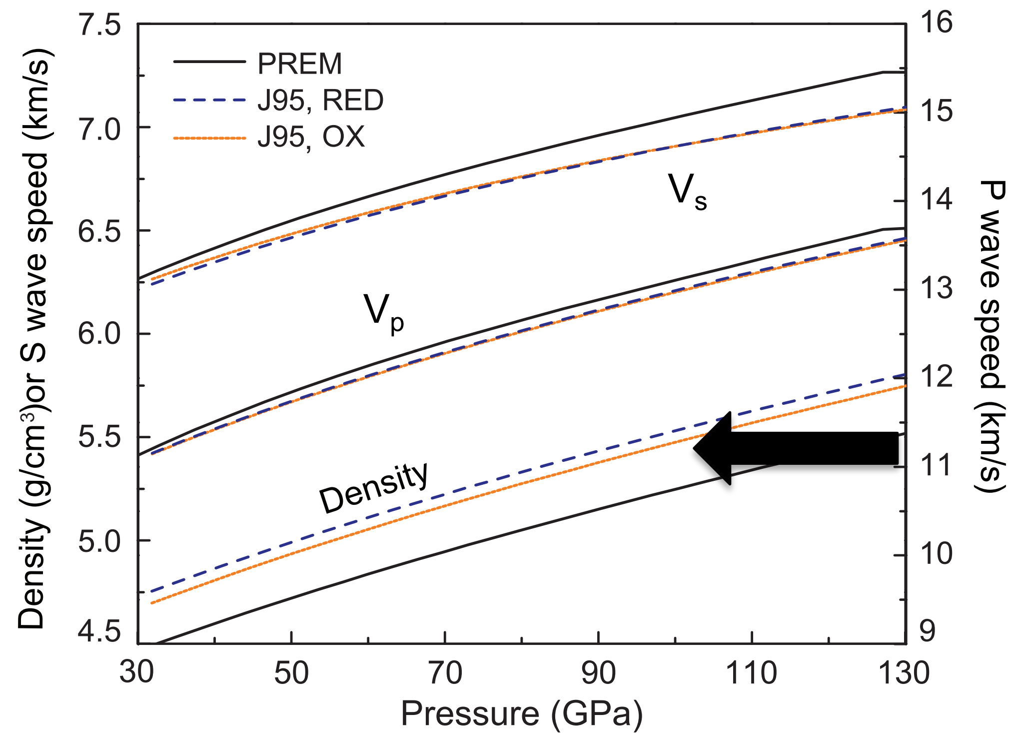
MIX_OX Bridgmanite composition:

$$\left(Mg_{0.51}Ca_{0.19}Fe^{2+}_{0.06}Al_{0.46}Fe^{3+}_{0.07}Si_{0.72}\right)O_3$$

V_0= 168.2 (±0.5) Å^3

Comparison with PREM





MIX1G

~1% density difference due to redox state!

Reduced: $Fe^{3+}/\Sigma Fe$ ~ 11%
Oxidized: $Fe^{3+}/\Sigma Fe$ ~ 55%

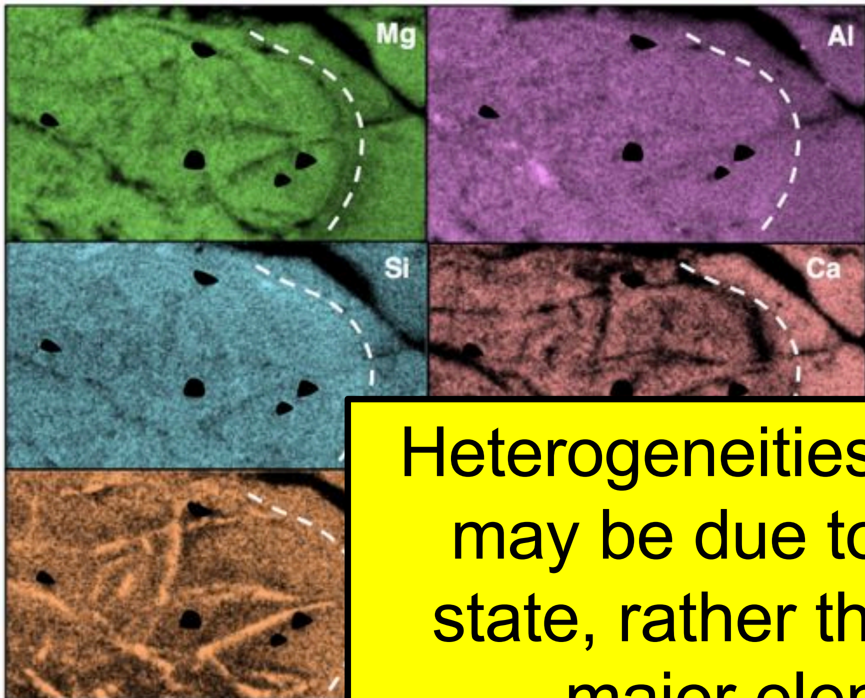
J95

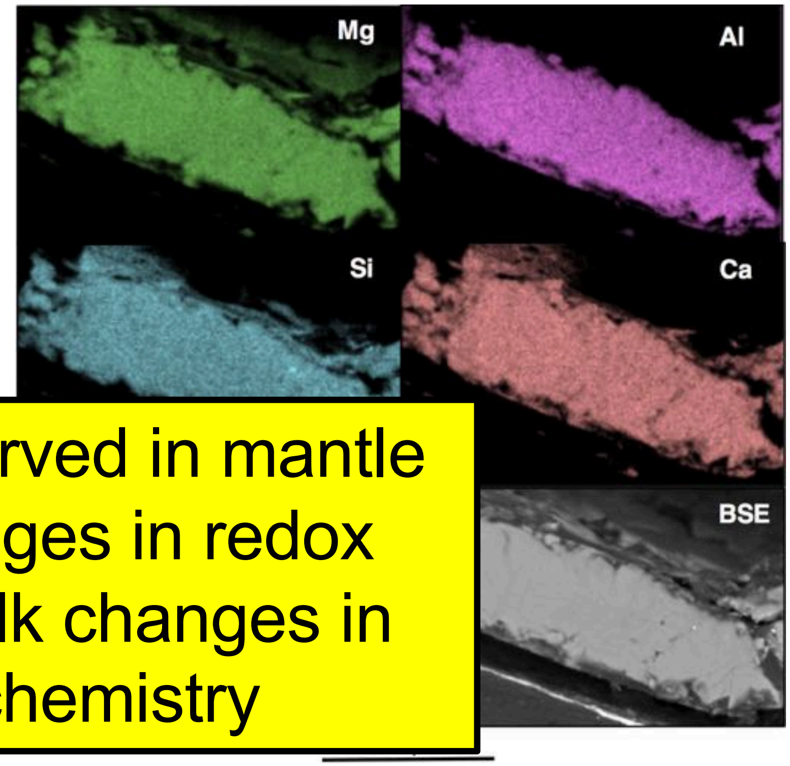
~1.5% density difference due to redox state!

Reduced: $Fe^{3+}/\Sigma Fe$ ~ 30%
Oxidized: $Fe^{3+}/\Sigma Fe$ ~ 35%

Creasy et al., *under review;* Gu et al., *Nature Geo, 2016*

Effect of Redox on Mantle Mineralogy





Heterogeneities observed in mantle may be due to changes in redox state, rather than bulk changes in major element chemistry

Reduced samples:

1. More complex mineralogy
2. Greater assemblage density

Oxidized samples:

1. Mostly bridgmanite
2. Lower assemblage density
3. Solid solution between Mg- and Ca-silicate perovskites

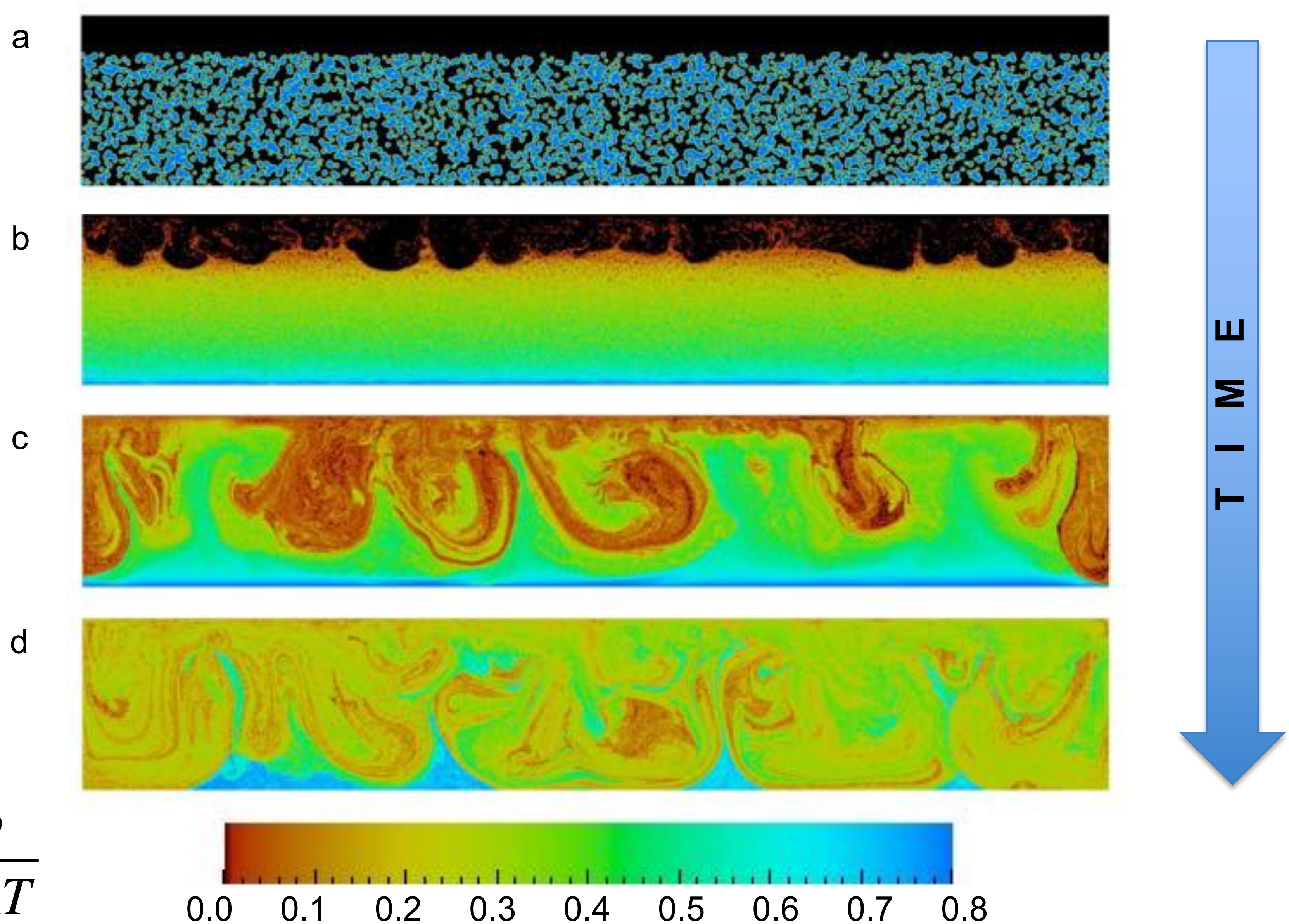
Creasy et al., *under review*

Geodynamic Modeling

Gu et al., *Nature Geo, 2016*

Model details described in Li et al., 2014

Geodynamic Modeling

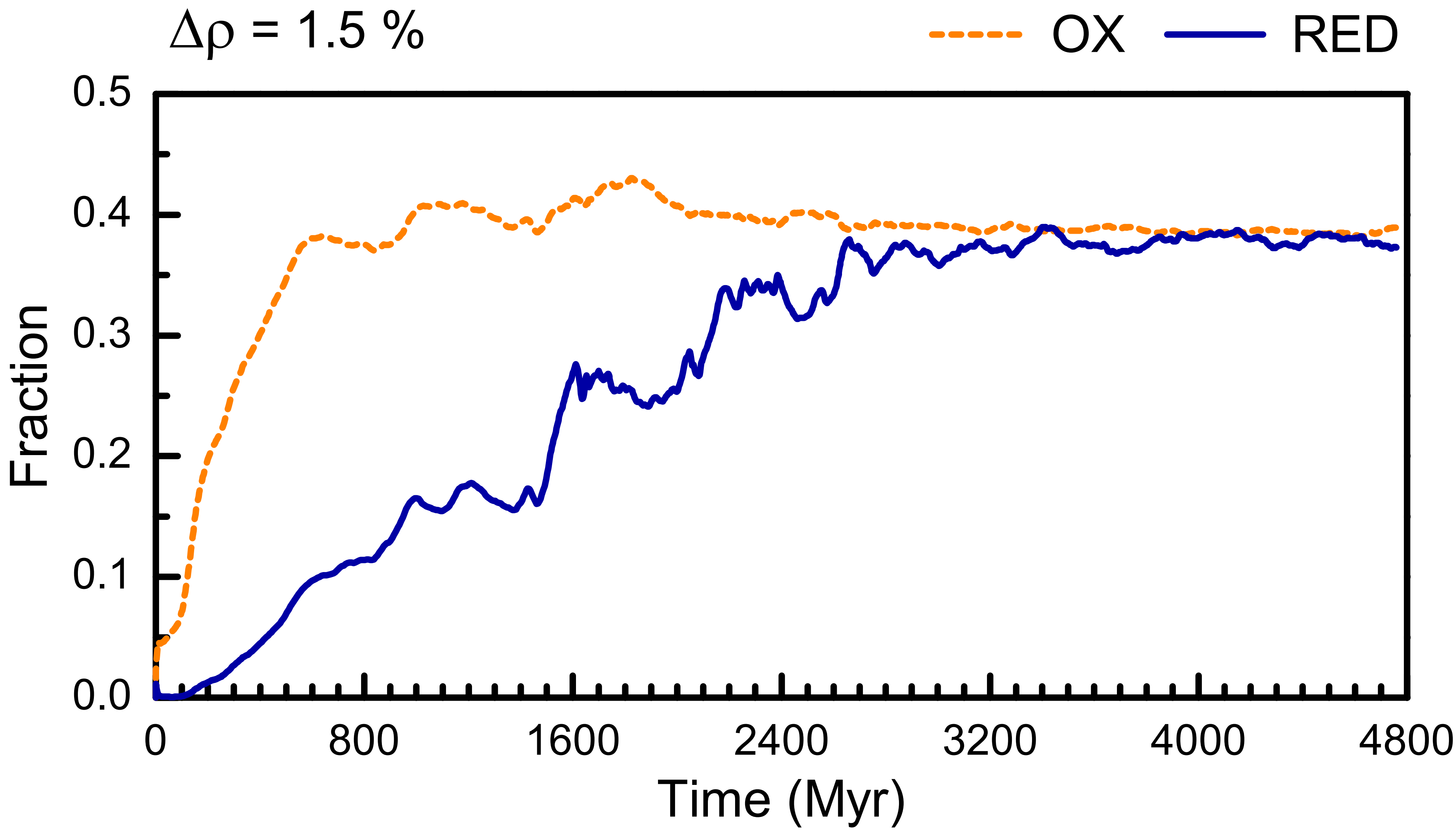


$$B = \frac{\Delta\rho}{\rho\alpha\Delta T}$$

Gu et al., *Nature Geo, 2016*

Model details described in Li et al., 2014

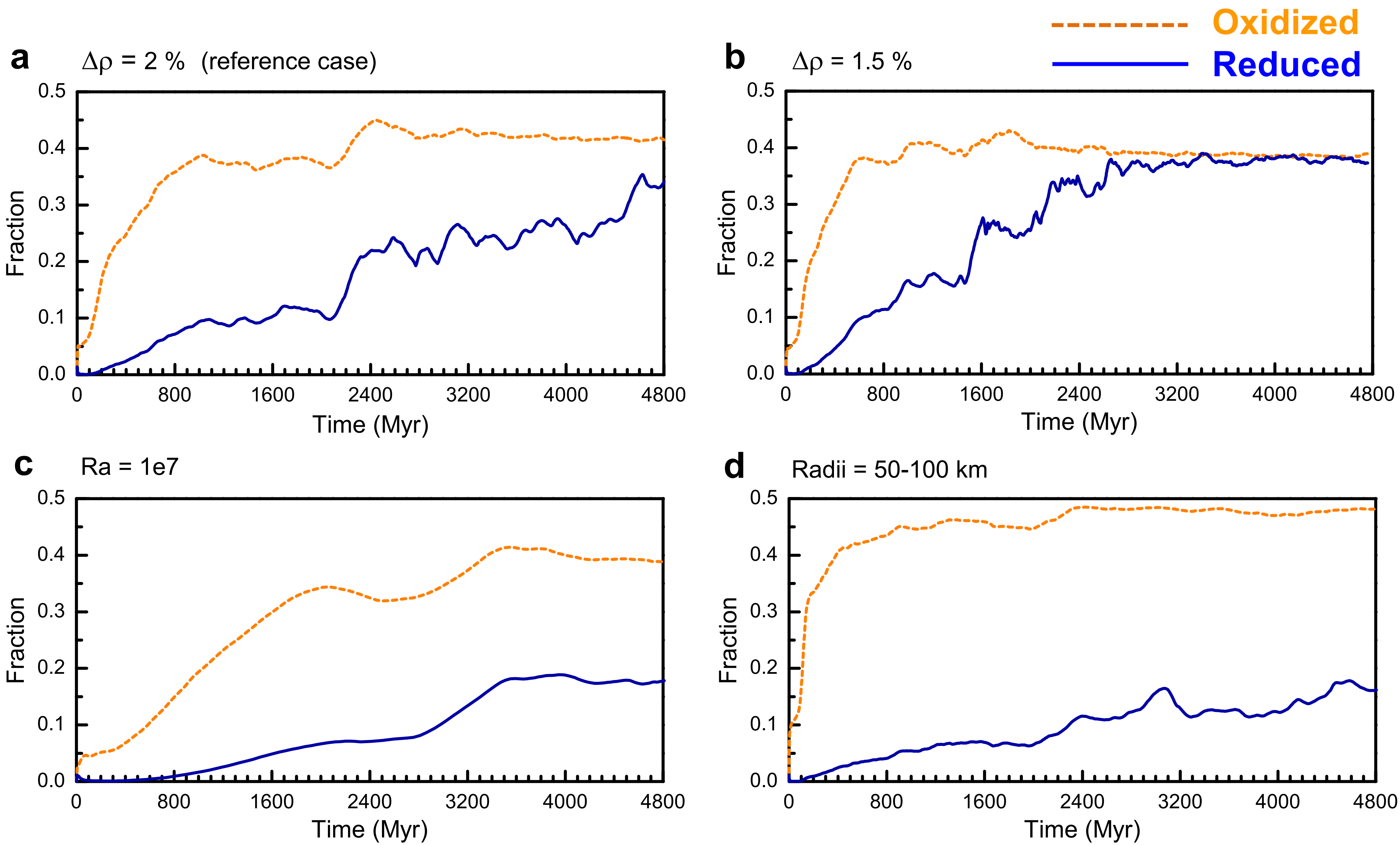
Evolution of upper mantle



Gu et al., *Nature Geoscience*, 2016

Model details described in Li et al., 2014

Evolution of upper mantle

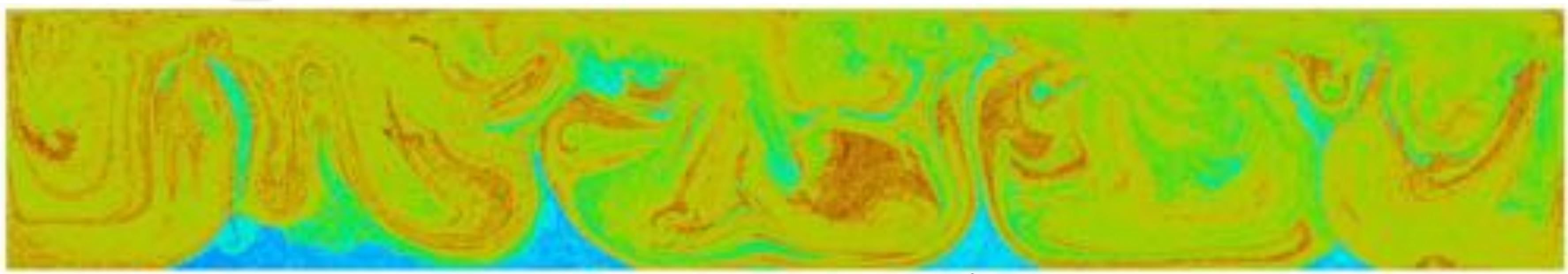


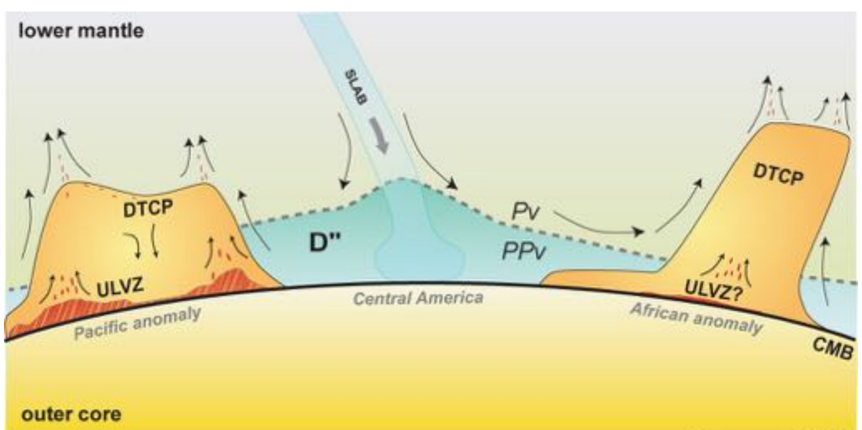
Gu et al., *Nature Geoscience*, 2016

Model details described in Li et al., 2014

What could this all mean?

Lots of O_2 in the atmosphere!



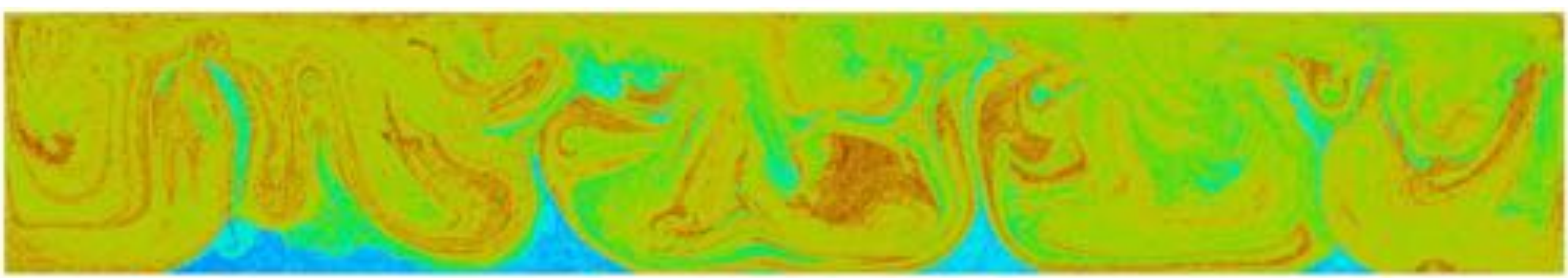


[Garnero et al. [2006]

Reduced, dense, *primordial* piles?

Summary

- Crystal chemistry in bridgmanite varies under different redox conditions influencing mantle mineralogy, density, seismic velocities and convection.
- More oxidized samples (high $Fe^{3+}/\Sigma Fe$), yield simpler assemblages and are less dense than their more reduced counterparts by ~1-2%.
- While there are several possible chemical models of the lower mantle, bridgmanite is nevertheless considered the dominant phase in the lower mantle; thus, its crystal chemistry has a leading role in the thermochemical evolution of the mantle (*and exosphere!*).



What comes next?

- How does Ca incorporation into bridgmanite affect partitioning of other large-ion lithophile elements (e.g., K, U, Th)?
- How are melting relations affected by redox state?
- What are the observables that can further test this hypothesis?
- What might this mean for planets beyond Earth, both within and outside of the Solar System?
- …